

THE RATE OF DISSOCIATION OF
PENTAARYLETHANES

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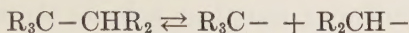


THE RATE OF DISSOCIATION OF PENTAARYLETHANES*

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In a previous paper¹ it was demonstrated that pentaarylethanes undergo reversible dissociation into free radicals, the position of equilibrium being nearly entirely in favor of the pentaarylethane.



From studies on the reaction of oxygen with solutions of the pentaarylethanes, it was concluded that the rate of oxygen absorption was a measure of the rate of dissociation of the pentaarylethane. It was found that at 100° pentaphenylethane dissociates into the triphenylmethyl and diphenylmethyl radicals approximately as rapidly as hexaphenylethane dissociates at 0°. From the velocity constants from the dissociation of pentaphenylethane at different temperatures, the energy of activation of the dissociation process was calculated to be 27.6 kcal., a value 50 per cent. greater than the corresponding value for hexaphenylethane.

If the rate of reaction with oxygen is actually a measure of the rate of dissociation of the pentaarylethane, then substantially the same rate of reaction should be observed with other reagents capable of reacting rapidly with the radicals formed on dissociation, and it was highly desirable that this point be tested. Accordingly, we decided to explore another reaction of this type, and we chose iodine as the reagent, since it is well-known that triarylmethyl radicals react rapidly with iodine as well as with oxygen. Preliminary experiments showed that at temperatures of 70–100° solutions of pentaphenylethane absorbed iodine, and the reaction appeared to be suitable for development as another method of determining the rates of dissociation.

For the reaction we employed a solution of iodine in a suitable solvent which contained some ethanol and pyridine, a mixture similar to that used by Ziegler, Ewald, and Orth² in their studies on the rate of dissociation of hexaarylethanes. The ethanol served to convert the triphenylmethyl iodide to triphenylmethyl ethyl ether as fast as it was formed; it was

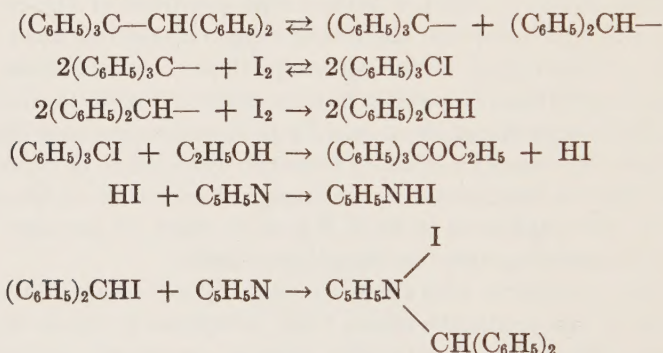
* From the ph.D. dissertation of Gerald Osborn.

¹ BACHMANN AND WISELOGLE, *J. ORG. CHEM.*, **1**, 354 (1936).

² ZIEGLER, EWALD, AND ORTH, *Ann.*, **479**, 277 (1930).

necessary to do this since the reaction of triphenylmethyl and iodine to give triphenylmethyl iodide is reversible. Pyridine was added to combine with the hydrogen iodide which is formed in the reaction giving the ether; this was done in order to prevent a reaction between the free radicals and the hydrogen iodide.

It was found that in the presence of ethanol and pyridine the radicals formed by dissociation of pentaphenylethane reacted with practically the theoretical amount of iodine; the final products proved to be triphenylmethyl ethyl ether and diphenylmethylpyridinium iodide. From this result it was apparent that the diphenylmethyl iodide formed by the union of the diphenylmethyl radical and iodine combined with the pyridine to give a quaternary salt in preference to forming an ether by reaction with the ethanol. The following equations indicate the reactions that take place when pentaphenylethane is employed.



Since it was necessary to work at a temperature of 80° or higher in order to have an appreciably rapid reaction, the choice of solvent was limited to those having boiling points above 100° when working at atmospheric pressure. Another requirement of the solvent was that it must not react with any of the compounds present in the reagent mixture. It was found that *o*-dichlorobenzene, bromobenzene, xylene, and α -bromonaphthalene were satisfactory solvents, while ethylene dibromide, anisole, and cyanobenzene were unsuitable. The rate of iodine absorption was determined by adding a weighed sample of the pentaarylethane to a measured volume of a solution of iodine in a solvent containing ethanol and pyridine. The reaction mixture was kept in a constant-temperature bath for a definite interval of time, then removed quickly and chilled. An excess of standard sodium thiosulfate solution was added to the mixture, and the excess was titrated with a standard solution of iodine. At a given temperature a series of samples identical in weight were run for different intervals of time, and an absorption-time curve was then plotted, from which the rate constant was determined.

In agreement with the results obtained on oxygen absorption, the rate-controlling step proved to be a reaction of the first order, corresponding to the unimolecular process of dissociation. Letting $Z = x/a$, the fraction of pentaphenylethane reacting, the equation for the first order reaction may be written:

$$k = \frac{-2.3}{t} \log (1 - Z)$$

Z was calculated as the ratio of the actual absorption of iodine to the theoretical absorption. When $-\log (1 - Z)$ was plotted against t , straight lines were obtained (Fig. 1); the slopes of the lines multiplied by 2.3 gave the velocity constants k . The data given in Table I show the

TABLE I

TYPICAL DATA OBTAINED IN REPRESENTATIVE EXPERIMENT

Wt. pentaphenylethane in each run, 0.1025 g.

o-Dichlorobenzene, 89.3%; pyridine, 4.7%; ethanol, 6.0%.

Theoretical absorption of 0.1 *N* iodine, 5 cc.

Temp., 94.9°.

TIME, MIN.	0.1 <i>N</i> IODINE ABSORBED, CC.	$-\log(1 - Z)$	Z FOUND	Z^* CALC'D ^a	DIFF.
1.0	0.31	0.0278	0.062	0.061	+0.001
2.0	0.56	0.0516	0.112	0.115	-0.003
3.0	0.90	0.0856	0.180	0.166	+0.014
4.0	1.07	0.1046	0.214	0.215	-0.001
5.0	1.33	0.1343	0.266	0.278	-0.012
6.1	1.54	0.1600	0.308	0.309	-0.001
8.0	1.95	0.2147	0.390	0.384	+0.006

^a Z^* calc'd is from the rate constant, 0.605, obtained from the curve (upper line, Fig. 1).

agreement between the actual results and those calculated on the basis of a first order reaction. The rate constant was found to be independent of the volume of solvent or concentration of iodine, as the results recorded in Table II indicate.

In Table III is presented a comparison of the velocity constants and half-life periods (t_1) for pentaphenylethane as determined by the iodine reaction and by the oxygen reaction. In both reactions *o*-dichlorobenzene was used as the solvent; however, pyridine and alcohol were present in the iodine reaction, while pyrogallol was present in the oxygen reaction. With due consideration for this difference, there is agreement between the two sets of values. A further comparison is obtained in the values of the energy of activation determined by the two reactions.

The energy of activation of the dissociation process was determined by

plotting $-\log k$ against $1/T$ in the customary manner (Fig. 2) and multiplying the slope of the line by $2.3R$. From the curves a value of 27.1 kcal. was obtained for the energy of activation by the iodine reaction, which is in good agreement with the value 27.6 kcal. obtained by the oxygen method.

TABLE II
EFFECT OF VARYING CONCENTRATIONS OF REAGENTS
Temp. 94.9°; solvent, *o*-dichlorobenzene

CONC. IODINE	CONC. PENTAPHENYLETHANE	RATE CONSTANT k
0.10 <i>N</i>	0.050 molar	0.0603
0.10	0.025	0.0605
0.05	0.025	0.0602

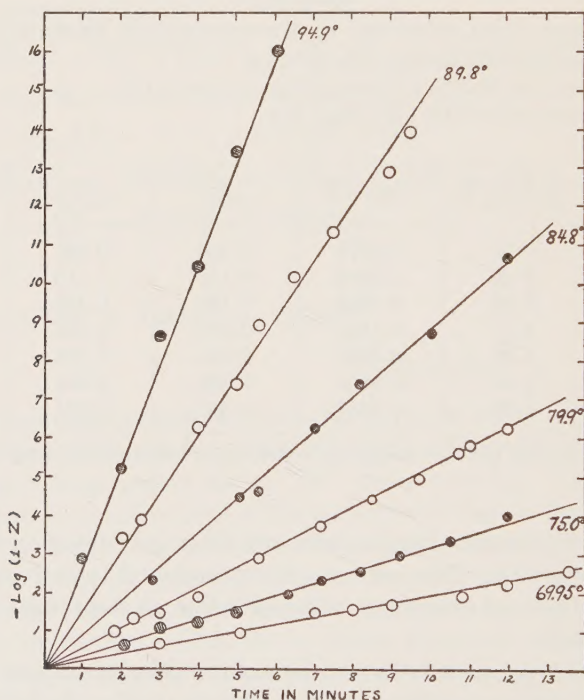


FIGURE 1.—IODINE ABSORPTION BY PENTAPHENYLETHANE IN *o*-DICHLOROBENZENE
 Z = fraction of pentaphenylethane reacting

The rate of dissociation of pentaphenylethane was determined not only in *o*-dichlorobenzene but also in xylene, bromobenzene, and α -bromonaphthalene. Although the specific rate constants varied in the different solvents, as is seen in Table IV, the value for the energy of activation

remained fairly constant, the average of the values obtained in the four solvents being 28.0 kcal.

With the successful development of a rapid and convenient method of measuring the rate of dissociation of a pentaarylethane, we were in a position to determine the effect of a series of aryl groups on the rate of dissociation. This was accomplished by measuring the rate of dissociation

TABLE III
RATE CONSTANTS AND HALF-LIFE PERIODS
Iodine reaction

Temp., °C.	69.95	75.00	79.90	84.80	89.80	94.90
k	.0042	.0075	.0122	.0205	.0339	.0605
t (min.)	165	92	56.7	33.8	20.4	11.4

Oxygen reaction

Temp., °C.	79.85	84.70	89.55	94.40	99.30	104.15
k	.0163	.0274	.0462	.0765	.1260	.2010
t (min.)	42.5	25.3	15.0	9.06	5.50	3.44

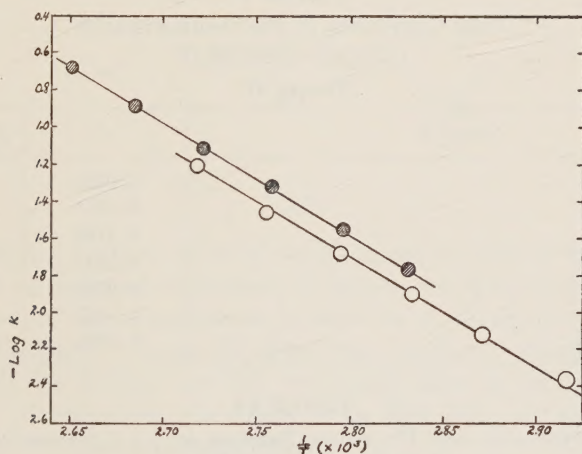


FIGURE 2.—Open circles: iodine reaction; $E = 27.1$ kcal. Shaded circles: oxygen reaction; $E = 27.6$ kcal.

of seven pentaarylethanes at the same temperature (80°) and in the same solvent. These pentaarylethanes all had the same general formula $(C_6H_5)_3C-CH(C_6H_5)R$ differing from one another only in the one group R . In Table V are shown the rate constants and half-life periods of the pentaarylethanes as determined by the iodine reaction. It is seen that the 9-phenanthryl, α -naphthyl and 2-fluoryl groups are most effective in

promoting a rapid dissociation, the *p*-biphenyl and *p*-anisyl groups have an intermediate effect, while the *p*-tolyl and phenyl groups are least effective. Work is now in progress to determine the effect of other groups

TABLE IV
ENERGY OF ACTIVATION OF PENTAPHENYLETHANE

SOLVENT		70°	75°	80°	85°	90°	95°	E (kcal.)
<i>o</i> -Dichlorobenzene	<i>k</i>	.0043	.0075	.0124	.0209	.0341	.0607	27.1
	<i>t</i> _½	161	92.4	56.0	33.2	20.3	11.4	
Xylene	<i>k</i>			.0111	.0198	.0345	.0575	28.1
	<i>t</i> _½			62.3	34.4	20.1	12.1	
Bromobenzene	<i>k</i>			.0108	.0216	.0361	.0575	28.5
	<i>t</i> _½			64.2	32.1	19.2	12.1	
α -Bromonaphthalene	<i>k</i>			.0123	.0225	.0407	.0690	28.4
	<i>t</i> _½			56.3	30.8	17.0	10.05	

TABLE V
RATE CONSTANTS OF PENTAARYLETHANES
(C₆H₅)₅C—CH(C₆H₅)R
Temp., 80°

GROUP, R	<i>k</i>	HALF-LIFE, MIN.
Phenyl.....	0.0124	56.0
<i>p</i> -Tolyl.....	0.0131	52.8
<i>p</i> -Anisyl.....	0.0166	41.8
<i>p</i> -Biphenyl.....	0.0241	28.8
2-Fluoryl.....	0.0404	17.2
α -Naphthyl.....	0.0437	15.9
9-Phenanthryl.....	0.0506	13.7

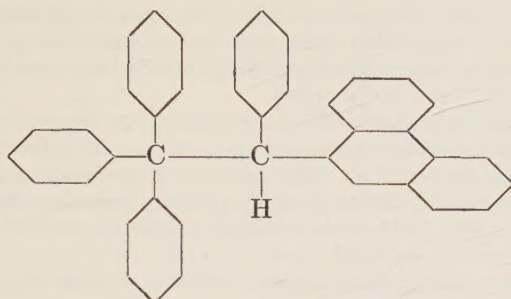
TABLE VI
RATE CONSTANTS AND HALF-LIFE PERIODS OF 1,1,1,2-TETRAPHENYL-
2-(9'-PHENANTHRYL)ETHANE

o-Dichlorobenzene, 89.5%; pyridine, 4.7%; ethanol, 5.8%

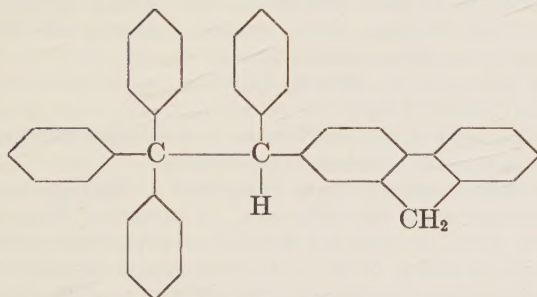
Temp., °C.....	65	70	75	80	85
<i>k</i>	.0094	.0154	.0308	.0506	.0828
<i>t</i>	73.7	45.0	22.5	13.7	8.4

in the molecule. When more data are at hand it will be apparent whether there is any correspondence between the effect of the groups in increasing the rate of dissociation of pentaarylethanes and in promoting the extent of dissociation of hexaarylethanes.

Two of the pentaarylethanes, 1,1,1,2-tetraphenyl-2-(9'-phenanthryl)ethane (I) and 1,1,1,2-tetraphenyl-2-(2'-fluoryl)ethane (II), are new; they were prepared by interaction of triphenylmethylsodium and the appropriate diarylmethyl chloride.



I



II

In view of the marked effect of the 9-phenanthryl group on the rate of dissociation of the pentaarylethane molecule, we determined the energy of activation of the dissociation process for 1,1,1,2-tetraphenyl-2-(9'-phenanthryl)ethane. Table VI shows the values of the rate constants and the half-life periods for this pentaarylethane in *o*-dichlorobenzene. The energy of activation was found to be 26.6 kcal., a value similar to that observed for pentaphenylethane.

EXPERIMENTAL

Phenyl-2-fluorylcarbinol.—Following the directions of Bachmann³, 5.4 g. of 2-benzoylfluorene⁴ was reduced by 60 g. of 2 per cent. sodium amalgam and 2.5 cc. of absolute alcohol in 25 cc. of anhydrous ether and 25 cc. of dry benzene. During the thirty minutes of shaking the solution became deep-blue and finally pale-green in color. The yield of recrystallized carbinol was 5.1 g. (94%); m.p. 113–114.5°. Ray and Levine⁵ reported a somewhat lower yield (82%), but slightly higher melting

³ BACHMANN, *J. Am. Chem. Soc.*, **55**, 770 (1933).

⁴ BACHMANN AND BARTON, *J. Org. Chem.*, **3**, 300 (1938).

⁵ RAY AND LEVINE, *Ibid.*, **2**, 273 (1937).

point (116°), for the carbinol obtained by reduction of the ketone by zinc dust and alcoholic ammonia or potassium hydroxide. The ketone gives a yellow color and the carbinol gives a deep-red color with concentrated sulfuric acid.

Phenyl-2-fluorylchloromethane.—A solution of 4.8 g. of phenyl-2-fluorylcarbinol in 50 cc. of benzene containing 2.5 g. of anhydrous calcium chloride was saturated with hydrogen chloride at 0°. After standing for twelve hours, the solution was filtered, and the benzene was evaporated under reduced pressure. Recrystallization of the residue from petroleum ether gave 4.6 g. (88%) of colorless crystals of the chloride; m.p. 122.5–123.5° (Ray and Levine, 122°).

Phenyl-2-fluorylbromomethane.—To a solution of 6 g. of phenyl-2-fluorylcarbinol in 6 cc. of benzene was added 2.5 cc. of acetyl bromide; the solution was warmed to its boiling point and then cooled. Upon addition of petroleum ether (60–70°), 6.7 g. (91%) of colorless crystals of the bromide precipitated; m.p. 128–129°. Ray and Levine⁶ obtained a 50% yield of the bromide melting at 118–119° by the action of hydrogen bromide on the carbinol.

1,1,1,2-Tetraphenyl-2-(2'-fluoryl)ethane (II).—A solution of triphenylmethylsodium was prepared from 2.79 g. of triphenylchloromethane and coupled with 2.91 g. of phenyl-2-fluorylchloromethane according to the procedure described previously¹. Recrystallization of the product from benzene gave 2.45 g. (49%) of fine, colorless crystals of the pentaarylethane. The compound melts at 152–162° in air and at 164–168° in nitrogen to an orange-colored liquid.

Anal. Calc'd for $C_{39}H_{30}$: C, 93.9; H, 6.1.

Found: C, 93.4; H, 6.0.

Nearly the same yield of pentaarylethane was obtained when phenyl-2-fluorylbromomethane was employed in place of the chloride.

The structure of the pentaarylethane was proved by cleavage by hydrogen iodide into triphenylmethane and 2-benzylfluorene. A mixture of 0.1 g. of iodine, 0.3 g. of red phosphorus, 0.2 cc. of water and 10 cc. of acetic acid was warmed for ten minutes; after addition of 0.25 g. of the pentaarylethane the mixture was refluxed for one hour in an atmosphere of nitrogen. The solution was filtered, and the filtrate was poured into a solution of sodium carbonate containing some sodium bisulfite. The products were extracted with benzene, the benzene solution was dried and then concentrated to a small volume. From the solution 90 mg. of triphenylmethane crystallized. By evaporation of the filtrate and solution of the residue in 30 cc. of hot alcohol and cooling, 55 mg. of 2-benzylfluorene was isolated in the form of colorless leaflets. The 2-benzylfluorene was found to exist in two forms; the crystals first melted at 94–95°, the melt solidified and remelted at 104–105.5°. The dimorphic state explains the wide range of melting points, varying from 99° to 106°, previously reported for this compound.

A sample of 2-benzylfluorene was prepared for comparison in the following manner. To 0.25 g. of phenyl-2-fluorylcarbinol was added 0.3 g. of red phosphorus, 0.1 g. of iodine, 0.2 cc. of water and 10 cc. of acetic acid. The mixture was refluxed for one hour and then worked up in the manner described for the cleavage reaction; yield, 0.19 g. (80%); m.p. 94–95°; 104–105.5°. When this material was mixed with the 2-benzylfluorene obtained in the cleavage reaction, the melting points remained unchanged.

Phenyl-9-phenanthrylcarbinol.—Eleven and three-tenths grams of 9-benzoylphenanthrene⁶ and 50 cc. of anhydrous isopropyl alcohol were added to the aluminum isopropoxide solution prepared from 1 g. of aluminum wire and 20 cc. of anhydrous

⁶ BACHMANN AND KLOETZEL, *Ibid.*, **2**, 363 (1937).

isopropyl alcohol according to the procedure of Lund⁷. The mixture was heated on a steam bath so that the acetone formed in the reaction was distilled off slowly with the isopropyl alcohol. When no more acetone could be detected in the distillate by means of 2,4-dinitrophenylhydrazine, the isopropyl alcohol was removed under reduced pressure, and the residue was treated with ice-cold dilute sulfuric acid. Recrystallization of the dried product from benzene-petroleum ether gave 10.6 g. (93%) of colorless crystals of the carbinol; m.p. 139–140°. The product was identical with the carbinol prepared by interaction of 9-phenanthrylmagnesium bromide and benzaldehyde⁸.

Phenyl-9-phenanthrylchloromethane.—A cold solution of 8.52 g. of phenyl-9-phenanthrylcarbinol in 70 cc. of dry benzene containing 3 g. of anhydrous calcium chloride was saturated with hydrogen chloride. After twelve hours at room temperature the benzene solution yielded 7.7 g. (85%) of fine, colorless needles of phenyl-9-phenanthrylchloromethane; m.p. 114–116°.

Anal. Calc'd for $C_{21}H_{15}Cl$: Cl, 11.7. Found: Cl, 11.6.

Phenyl-9-phenanthrylbromomethane.—A mixture of 5.9 g. of phenyl-9-phenanthrylcarbinol and 2.4 cc. of acetyl bromide was heated on a steam bath for one-half hour. The acetic acid was removed under reduced pressure, and the residual oil was dissolved in a mixture of warm benzene and ligroin. On cooling, 6.87 g. (95%) of the bromide crystallized in clusters of colorless plates; m.p. 115–116°.

Anal. Calc'd for $C_{21}H_{15}Br$: Br, 23.0. Found: Br, 22.6.

1,1,1,2-Tetraphenyl-2-(9'-phenanthryl)ethane (I).—This pentaarylethane was obtained in 80% yield by reacting a solution of 3.03 g. (0.01 mole) of phenyl-9-phenanthrylchloromethane in 5 cc. of benzene with an ice-cold solution of triphenylmethylsodium (0.01 mole) in the customary manner¹. After recrystallization from benzene the compound melted at 176–188° in air and at 190–193° in nitrogen to a reddish-orange liquid.

Anal. Calc'd for $C_{40}H_{30}$: C, 94.1; H, 5.9.

Found: C, 93.8; H, 5.7.

A 0.25-g. sample of the pentaarylethane was cleaved by hydrogen iodide according to the procedure described for the 2-fluoryl derivative. The mixture of the two methanes, triphenylmethane and 9-benzylphenanthrene, was dissolved in 4 cc. of 90–100° petroleum ether; on being cooled slightly the solution deposited 45 mg. of 9-benzylphenanthrene; m.p. 155–156°, alone and when mixed with an authentic specimen. The filtrate was evaporated and the residue dissolved in hot benzene; from the solution 55 mg. of triphenylmethane crystallized.

Reaction between pentaphenylethane and iodine.—A solution of 0.4 g. of pentaphenylethane, 0.2 g. of iodine, 1 cc. of absolute alcohol, 1 cc. of pyridine, and 10 cc. of benzene was refluxed on a steam bath. After two and one-half hours the iodine color had practically disappeared. On cooling, 0.48 g. of yellow crystals precipitated; by recrystallization from water 0.37 g. of diphenylmethylpyridinium iodide was obtained as yellow prisms. The salt had no definite melting point; it decomposed between 162° and 194°.

Anal. Calc'd for $C_{18}H_{16}NI$: I, 34.0. Found: I, 33.9.

The benzene filtrate from the diphenylmethylpyridinium iodide was evaporated, and the residue was dissolved in hot petroleum ether. After removal of 40 mg. of precipitated pentaphenylethane, the solution was concentrated and cooled, whereupon 0.26 g. of triphenylmethyl ethyl ether crystallized.

⁷ LUND, *Ber.*, **70**, 1520 (1937).

⁸ BACHMANN, *J. Am. Chem. Soc.*, **56**, 1366 (1934).

Diphenylmethylpyridinium iodide.—To a solution of 5 g. of sodium iodide in 50 cc. of acetone was added 10 cc. of an acetone solution of 3.14 g. of diphenylbromomethane. After one hour the sodium bromide was removed by filtration, and 10 cc. of pyridine was added to the clear solution of diphenyliodomethane. After twelve hours the acetone and pyridine were removed in a current of air, and the solid residue was recrystallized from hot water, yielding 3.9 g. (89%) of diphenylpyridinium iodide as yellow prisms; m.p. 162–194° with decomposition.

Anal. Calc'd for $C_{18}H_{16}NI$: I, 34.0. Found: I, 33.9.

Rate measurements.—The pentaarylethanes were dried for several hours in high vacuum at 80–100°; the purity of the samples was established by analysis for carbon and hydrogen. The iodine solution was made up by adding *o*-dichlorobenzene (or other solvent) to a solution of 6.5 g. of iodine in 32.5 cc. of pyridine until the total volume was 500 cc. The samples (0.1025 g. each) of pentaphenylethane were weighed into glass vials, 12 mm. deep and 8 mm. in diameter, having flat bottoms. Ten cubic centimeters of the iodine solution and 1 cc. of absolute alcohol were placed in a 125-cc. Erlenmeyer flask bearing a glass stopper. The flask was suspended in a water bath kept at the desired temperature to within 0.05°. The vial containing the sample of pentaphenylethane was then lowered in an upright position into the Erlenmeyer flask by means of forceps and allowed to float on the surface of the organic solution of iodine. The flask after being stoppered loosely was allowed to reach the temperature of the bath, for which ten minutes proved to be sufficient. The vial was then tipped over by swirling the flask, a stop-watch being started at this time; the pentaphenylethane dissolved very rapidly. When the desired interval of time had elapsed, the flask was removed quickly from the bath and immersed in ice-water, the watch being stopped at this point.

Ten cubic centimeters of sodium thiosulfate solution, slightly stronger than 0.1 *N* (strong enough to react with all the iodine originally present in the organic solution), was added, 50 cc. of water was used to rinse down the sides of the flask, and the excess of sodium thiosulfate was titrated with a standardized 0.1 *N* solution of iodine in potassium iodide and water. From the volume of this standard iodine solution needed to give the end-point with starch was subtracted the volume of iodine solution required to give the end-point to a blank. The latter was run with all of the reagents present except the pentaphenylethane in exactly the same manner as the regular run. The difference was the volume of 0.1 *N* iodine which reacted with the radicals formed by dissociation of the pentaphenylethane. It is apparent that the strength of only the aqueous solution of iodine must be known accurately. The other pentaarylethanes were run in the same manner.

The presence of an appreciable amount of the diarylmethyl-pyridinium iodide in the water solution interfered with the end-point; for this reason the reactions were not allowed to proceed to any great extent. It is believed that the results which were obtained are in error by no more than 5 per cent.

SUMMARY

Solutions of pentaarylethanes readily absorb iodine at 70–100° in the presence of ethanol and pyridine. It has been shown that the reaction proceeds through the intermediate formation of free radicals produced by dissociation of the pentaarylethane. The products that are formed under these conditions are triarylmethyl ethyl ethers and diarylmethylpyridinium iodides.

A rapid and convenient method was developed for determining the rate of dissociation of pentaarylethanes.

The energy of activation for the dissociation of pentaphenylethane was determined in four different solvents. The energy of activation for the dissociation of 1,1,1,2-tetraphenyl-2-(9'-phenanthryl)ethane was also determined.

The rate of dissociation at 80° of seven different pentaarylethanes was measured. From the results a comparison of the effect of seven aryl groups on the rate of dissociation was obtained.

